

## Attachment 141

Central Research and Development  
Corporate Center for Analytical Sciences  
Experimental Station

DuPont EDL  
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BMP 14/286  
TRC E323/3309

January 21, 2009

TO: J. R. Hoover, FLPR, CRP 702/2116  
FROM: A. D. English *AME*

### SUBLIMATION OF PROCESSING AIDS FRD-903K AND FRD-902

Please find attached a copy of an Analytical Report entitled "Gas Phase Migration of FRD-903K and FRD-902 Under Ambient Conditions." This Analytical Report documents work done to address the issue of sublimation of FRD-903K and FRD-902 under ambient conditions. The report concludes that the FRD-903K and FRD-902 can migrate as a molecule containing the entire backbone with an unknown counter-ion ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{COOX}$ ; X not defined) inside an infrared spectroscopy gas cell resulting in reaction product formation on the alkali salt windows. Note that this conclusion deals with migration, not sublimation.

Differentiation between sublimation and migration is a subtle and often confused subject. There are many papers in the literature dealing with sublimation; however, two papers deal with the sublimation of  $\text{NH}_4\text{Cl}$ .<sup>1,2</sup> These papers indicate that the salt undergoes a chemical reaction to make  $\text{NH}_3$  and  $\text{HCl}$  and these two gases then vaporize. In the strictest sense this is not a sublimation, but a chemical reaction; however, the authors of both papers refer to this as sublimation. This is relevant to the current case because while the data is most consistent with the transporting species being dimer acid (formed from a reaction of the salt with water) and in this case this would not be, strictly speaking, sublimation, but rather a chemical reaction followed by transport; however, this hypothesis has not been rigorously proven and the alternative hypothesis would be direct sublimation.

The conclusion that the transporting species is either the acid ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{COOH}$ ) or one of the salts ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{COOX}$ ; = K or  $\text{NH}_4$ ) is valid.

### References

1. "Rate of Sublimation of Ammonium Halides" Chaiken, R. F.; Sibbett, D. J.; Sutherland, J. E.; Van de Mark, D. K.; Wheeler A. *J. Chem. Phys.* 1962 37(10), 2311.
2. "Sublimation of Ammonium Salts: A Mechanism Revealed by a First-Principles Study of the  $\text{NH}_4\text{Cl}$  System" Zhu, R. S.; Wang, J. H.; Lin, M. C. *J. Chem. Phys.* 2007 111, 13831.



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January 19, 2009

Analytical Report

TO: A. D. English  
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Gas Phase Migration of FRD-903K and FRD-902 Under Ambient Conditions

Abstract

FRD-903K and FRD-902 were characterized in terms of their migration behavior under ambient conditions. It has been demonstrated that the potassium and ammonium salts of dimer acid (FRD-903) can migrate as a molecule containing the entire backbone with an unknown counter-ion ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{COOX}$ ; X not defined) inside an infrared spectroscopy gas cell resulting in reaction product formation on the windows. The most likely mechanism for this migration is generation of small amounts of dimer acid from the salts reacting with water. The dimer acid has significant vapor pressure and migrates through the gas phase, arrives at the gas cell window and reacts with the alkali metal salt to produce a salt reaction product on the window. This most likely, but not rigorously proven, mechanism is formally not sublimation, but rather a chemical reaction involving the equilibrium of the salt with dimer acid and the conjugate base ( $\text{KOH}$  or  $\text{NH}_4\text{OH}$ ), followed by vaporization of the acid (which has a significant vapor pressure) and migration to the window where it can react to produce the salt as a reaction product on the window.

Request/Need

The question of sublimation of FRD-902 and FRD-903K has been raised. Direct determination of the hypothesized transport of these materials through the gas phase was required.



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Background, Results and DiscussionReference Data

Figure 1 shows the reference infrared absorption spectra of four relevant materials, FRD-903 (dimer acid), the dehydrate of FRD-902 (ammonium salt solution), the dehydrate of FRD-903K (potassium salt solution), and E1 (decarboxylated FRD-903). These spectra were obtained via attenuated total reflectance (ATR) on the pure materials deposited onto a non-reactive diamond ATR element. The spectra were corrected for the ATR effect on intensities. The characteristic bands in these spectra include a multiplet between  $900\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  which arises from C-F stretching and bending modes associated with the fluorocarbon backbone in the molecules ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{COOX}$ ;  $\text{X}=\text{H}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ). For the free acid (FRD-903) there is a carbonyl stretch at  $1770\text{ cm}^{-1}$ . In the salt forms, this mode shifts to lower frequency since it is in the carboxylate form. In the potassium salt a doublet is observed at  $1675\text{ cm}^{-1}$  and  $1693\text{ cm}^{-1}$  and in the ammonium salt a single peak is found at  $1716\text{ cm}^{-1}$ . The ammonium salt also shows a N-H scissoring mode at  $1630\text{ cm}^{-1}$ . The E1 shows no modes above  $1400\text{ cm}^{-1}$ .

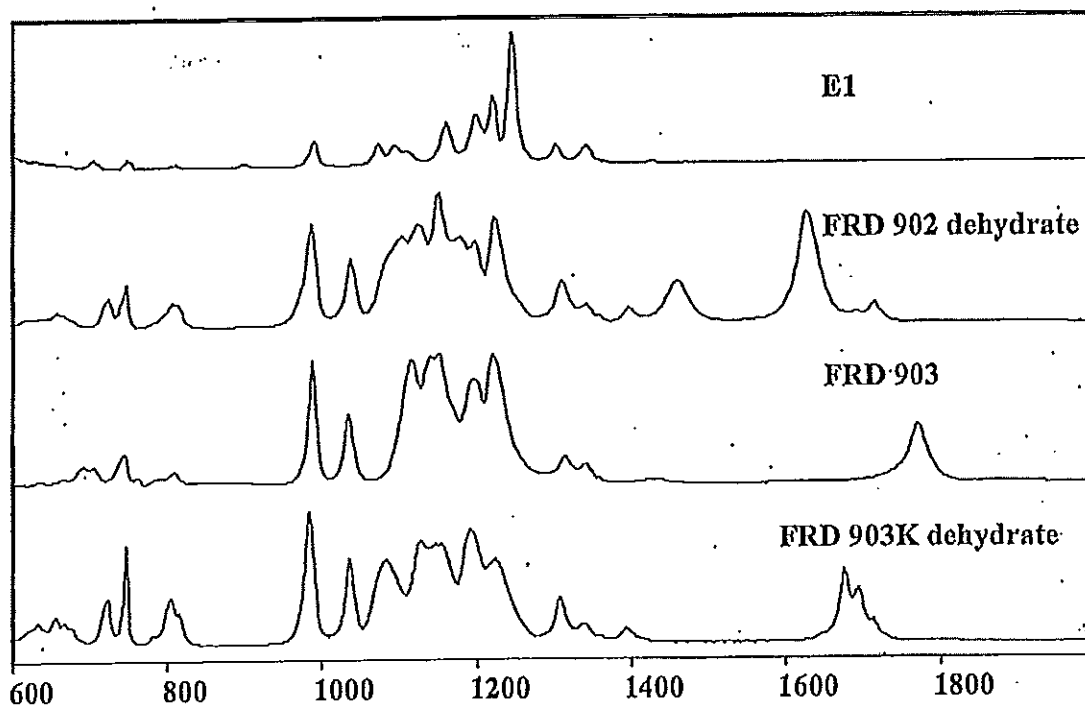
**Infrared Absorption Spectra Reference Materials**

Figure 1

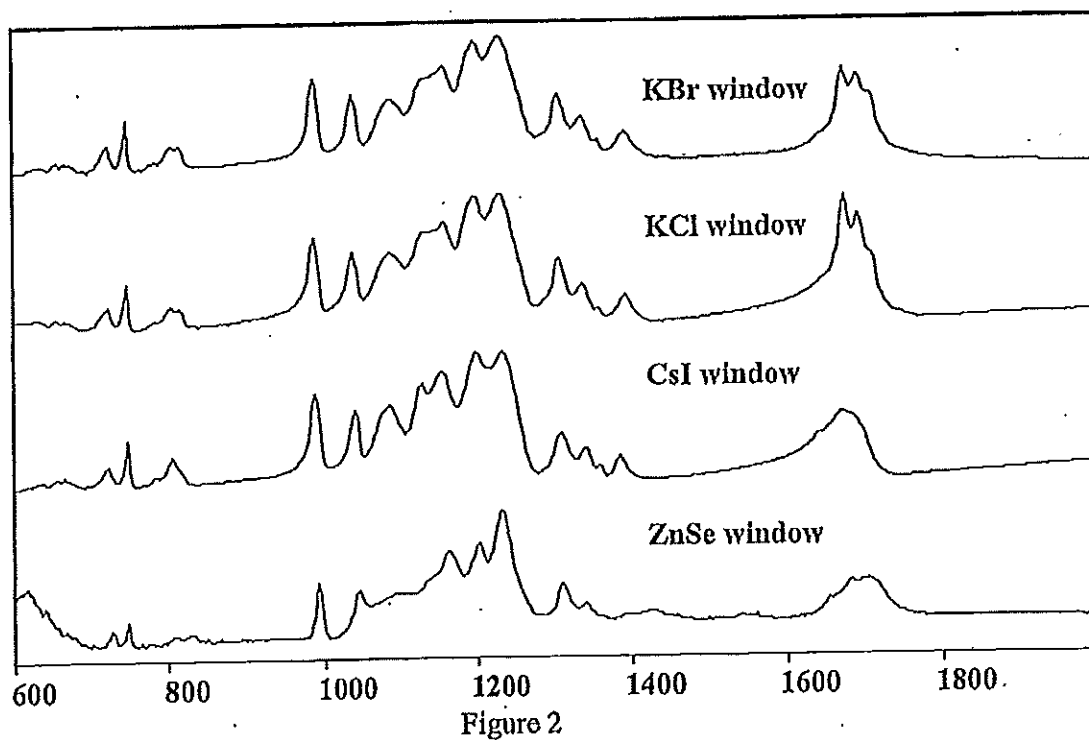
When dimer acid (FRD-903) is placed on various alkali halide and also zinc selenide windows a reaction takes place resulting in salt formation. Figure 2 shows the spectra of the salt formed by acid reaction with various window materials. The characteristic C-F stretching and bending modes are seen from  $900\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$ , and the carboxylate stretching mode is seen near  $1700\text{ cm}^{-1}$ . The spectrum of the reaction product of FRD-903 on a potassium bromide



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window (Figure 2) is a good match to the reference spectrum of the dehydrate of the aqueous solution of the potassium salt (FRD-903K) on an ATR crystal (Figure 1). Furthermore, the spectra of the reaction products on the other infrared windows show subtle shifts in the carboxylate stretching mode due to the effect of a change in counter ion from potassium to cesium to zinc. When the dimer acid (FRD-903) is placed on infrared window materials that are resistant to chemical attack by acid, there is no evidence for carboxylate salt or reaction product on the window. This is shown for germanium and silicon windows in Figure 3.

#### Dimer Acid Deposited on Various Windows



## Dimer Acid Deposited on Various Windows

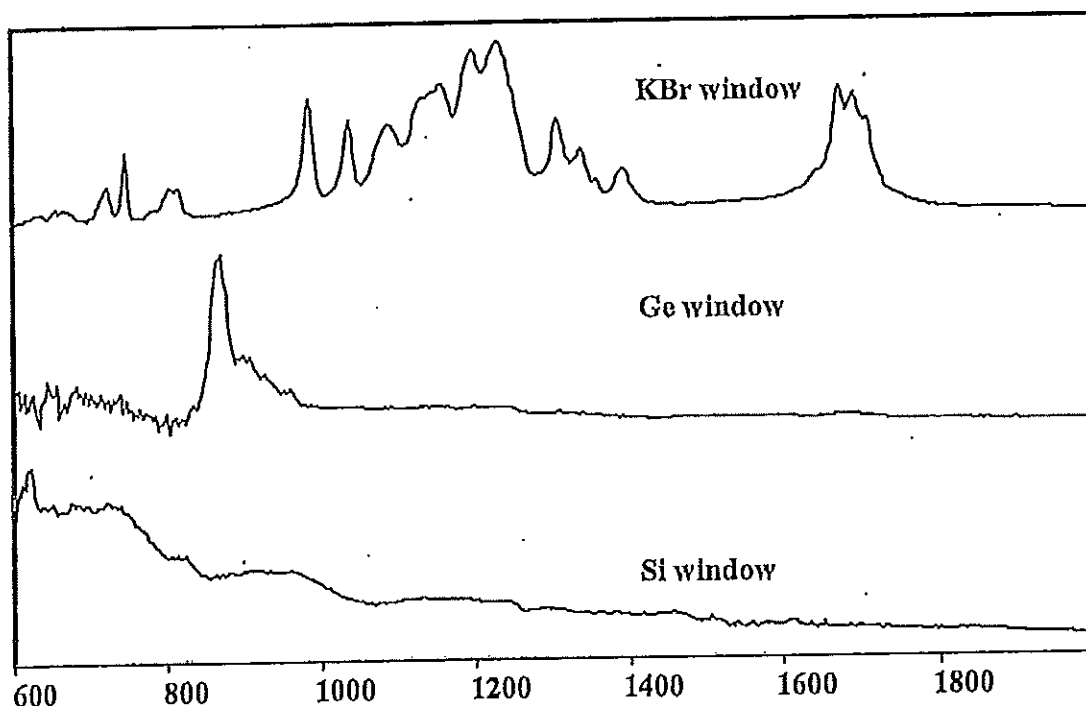


Figure 3

Transport Experiments

A sample of the dehydrate of the aqueous solution of the ammonium salt (FRD-902) (obtained from M. A. Kaiser) was placed in an infrared gas cell (KBr windows) and allowed to sit at room temperature for 6 hours. Infrared spectra taken during this time showed the evolution of water vapor. The gas cell was then purged with nitrogen and another infrared spectrum was acquired. This spectrum is shown in Figure 4 along with a reference spectrum of the reaction product obtained when a potassium bromide window was exposed to dimer acid (FRD-903). The spectra are quite similar, indicating that the transport of the fluorocarbon backbone of the ammonium salt occurred; the most likely, but not only, explanation is that the transporting species is the acid formed by reaction of the salt with adventitious water. Figure 5 shows similar results when FRD-902 (aqueous solution) was placed in the cell. After six hours, the cell was purged and the same reaction product spectrum was observed.

When zinc selenide windows were used, and the dehydrate of the aqueous solution of the ammonium salt was placed in the gas cell, the spectrum shown in Figure 6 was obtained. For comparison purposes, the reference spectrum for the FRD-903 reaction product on a zinc selenide window is shown. The gas cell reaction product matches very well with the dimer acid reaction product on zinc selenide.

An aqueous solution of potassium salt (FRD-903K) was placed in the gas cell (KBr windows) and allowed to sit for 6 hours. After purging the water vapor from the cell with nitrogen, the reaction product spectrum shown in Figure 7 was obtained. It also compares well with the reference spectrum of dimer acid on KBr windows.



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Dehydrate of Aqueous Solution of the Ammonium Salt KBr Gas Cell

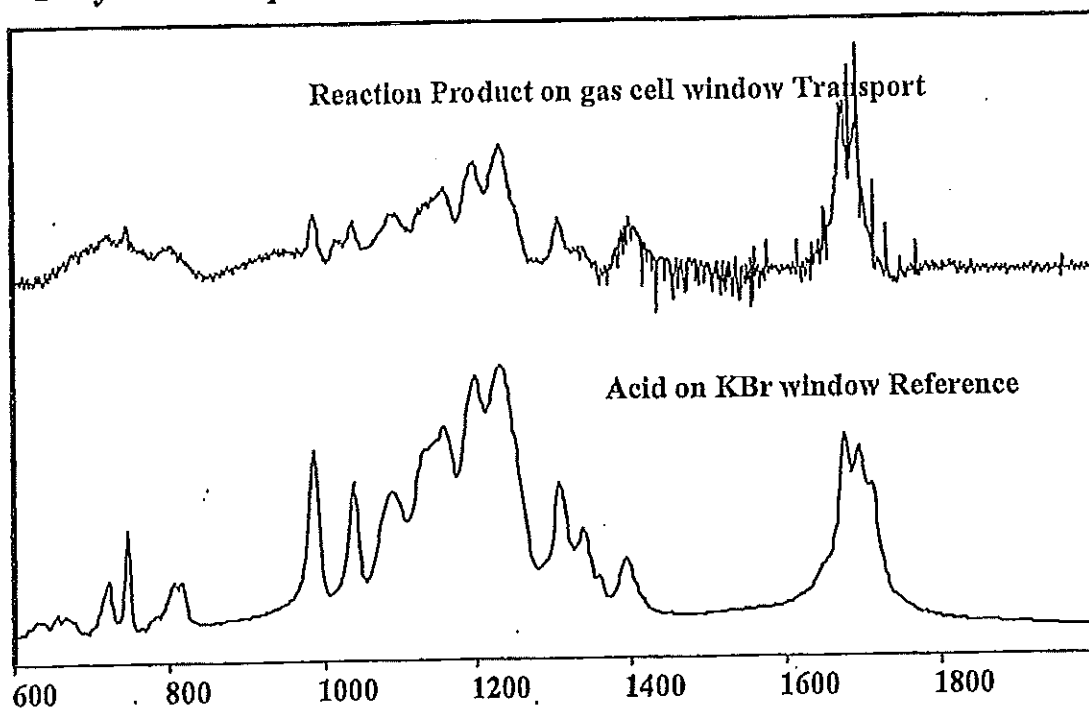


Figure 4

Ammonium Salt (solution) KBr gas cell

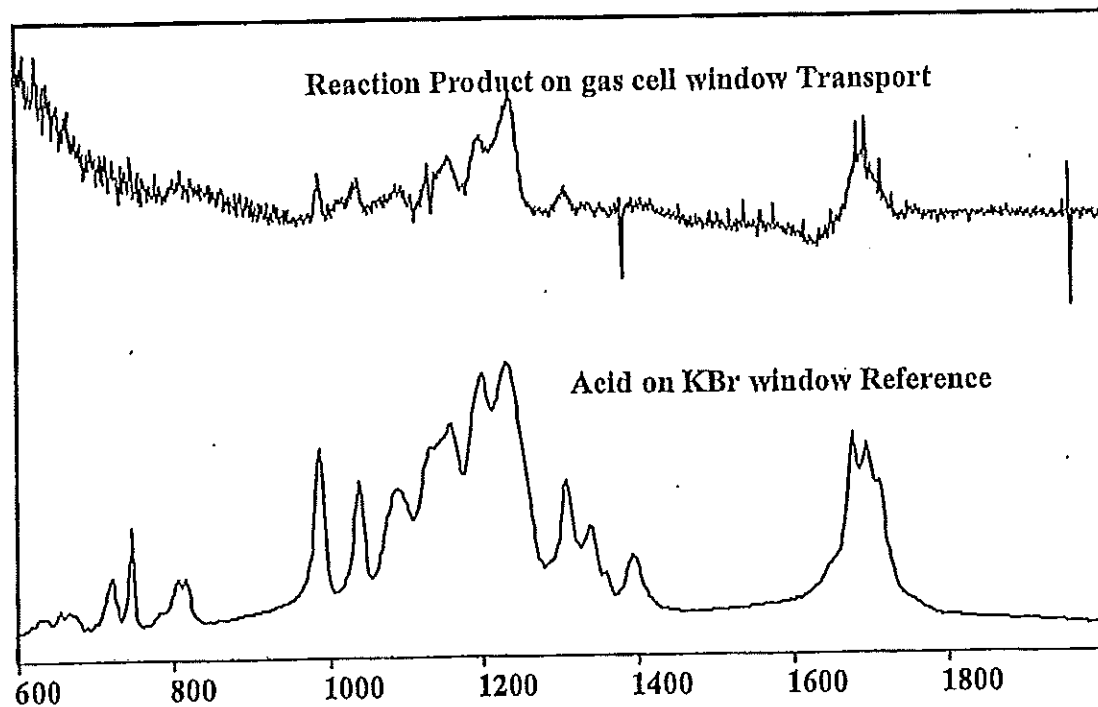


Figure 5



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Dehydrate of Aqueous Solution of the Ammonium Salt ZnSe Gas Cell

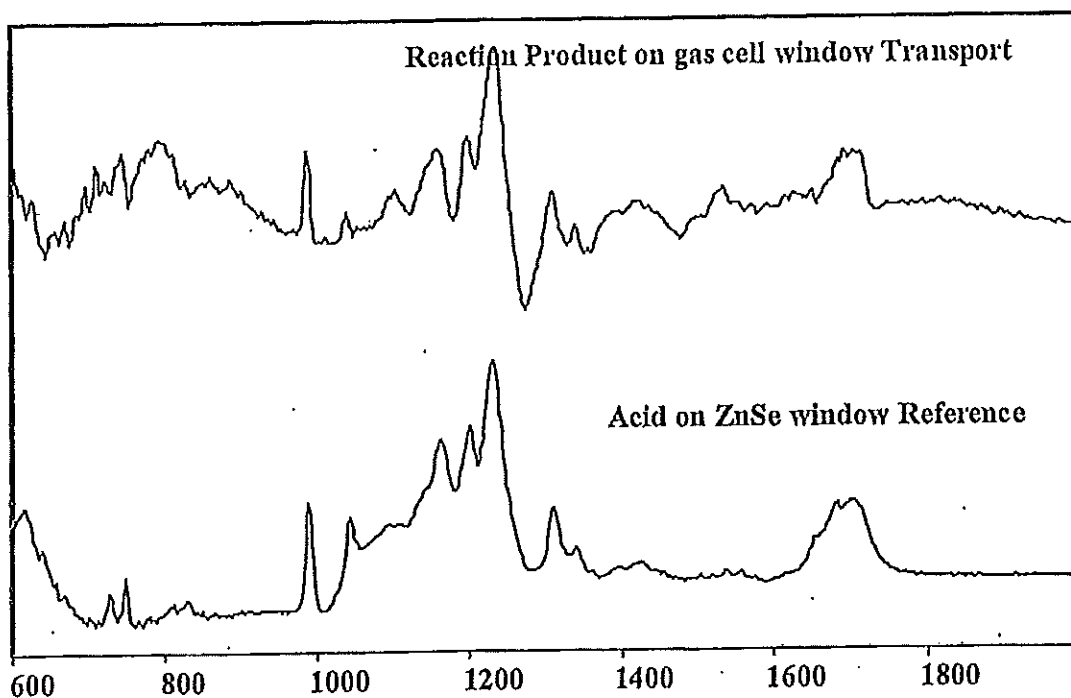


Figure 6

K salt (solution) KBr gas cell

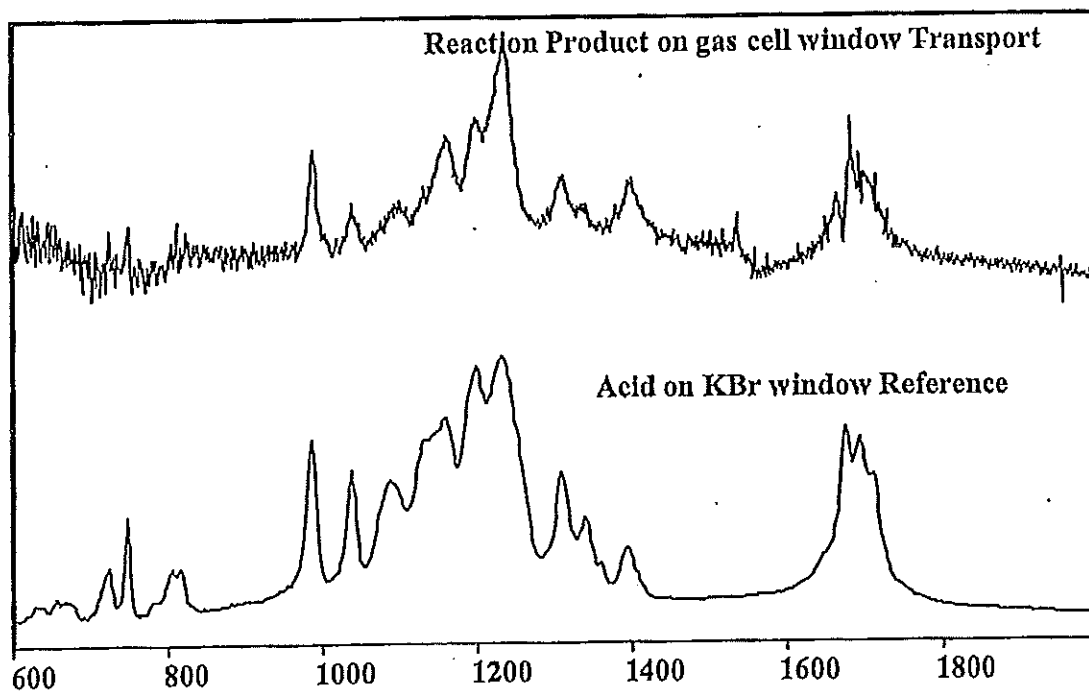


Figure 7



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The observation of the various reaction products formed in the transport experiments supports the hypothesis that salt forms of dimer acid, whether in solution or as dehydrates, can have their fluorocarbon backbone transported through the gas phase. The most likely mechanism is that the salt of dimer acid in the presence of (residual) water is in an equilibrium with dimer acid and the conjugate base (KOH or  $\text{NH}_4\text{OH}$ ). This acid has a significant vapor pressure and migrates to the window where it can react to produce the salt as a reaction product on the window. However, an alternative mechanism could be the direct transport of the salt to the window (sublimation) followed by an ion exchange reaction. This latter mechanism could only be excluded by direct observation of dimer acid in the gas phase originating from a salt.

In an attempt to differentiate between these two mechanisms an additional experiment was carried out. Since water ( $\text{H}_2\text{O}$ ) vapor often obscures the spectral features of interest for the fluorocarbon backbone, a sample of the dehydrated ammonium salt was dissolved in  $\text{D}_2\text{O}$  and dried to produce a solid with much lower  $\text{H}_2\text{O}$  content. This material was placed in the gas cell and after purging with nitrogen gas, the sample was allowed to sit for 24 hours.

### Dehydrate of Deuterated Ammonium Salt

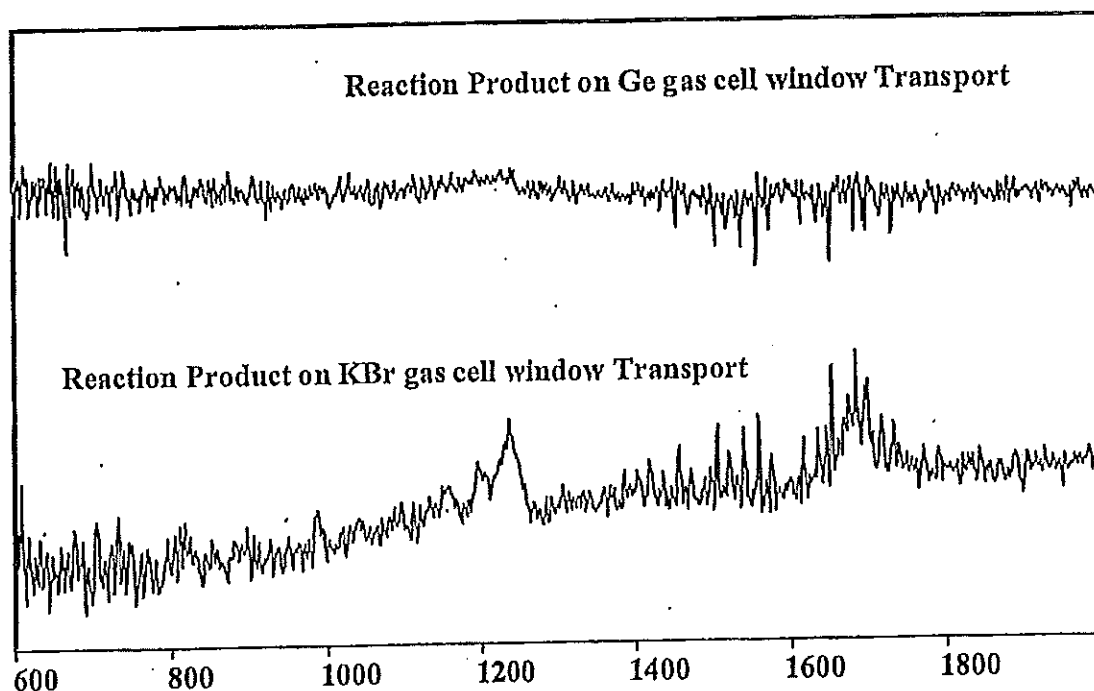


Figure 8

The lower trace in Figure 8 shows the results when KBr windows were used on the cell. The spectrum is identical to the one observed previously when the dehydrate of the ammonium salt was used (Figure 4). However the absolute intensities are weaker indicating less material on the window and there was no indication of vapor phase  $\text{D}_2\text{O}$ . It appears that this sample made via lyophilization of a  $\text{D}_2\text{O}$  solution had much less water in the solid; evidently less water in the sample retards the process of depositing reactant on the window either by decreasing the amount



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of material in the gas phase, or decreasing the reactivity at the window. This observation favors, but does not prove, the original hypothesis that the salt of dimer acid undergoes a reaction with residual water in the system, resulting in the generation of dimer acid which is then transported as a vapor to the salt window where it reacts with the KBr window. Note that since we are not able to directly characterize the gas phase species, we can not definitively rule out sublimation, but it seems unlikely based upon the evidence to date.

The upper trace in Figure 8 shows the spectrum obtained when Ge windows were used. There is no indication of reaction product on the window and no indication of any gas phase species. The absolute concentration of the gas phase species is too low to detect, indicating that the equilibrium between the solid and the gas phase species strongly favors the solid. Nevertheless, when there is a reactive sink, such as KBr, the gas phase material continues to react and deposit on the window, building up sufficient material to observe the spectrum.

### Experimental

All infrared spectra were recorded on a Nicolet 760 Magna FT-IR operating at  $4\text{ cm}^{-1}$  resolution. 256 scans were co-added. The preparation of the reference reaction product samples was done by placing a drop of dimer acid on the window and allowing it to evaporate. The gas cell experiments involved taking a standard ten cm gas equipped with a glass finger for sample introduction. The sample of interest was placed in the gas cell, and then the cell was purged with dry nitrogen for 5 minutes. The gas cell was then sealed and allowed to sit for six hours. The cell was then again purged with dry nitrogen to remove the water vapor, sealed again and the infrared spectrum of the windows was acquired.

One gram of the dehydrate of the solution of the ammonium salt of dimer acid was dissolved in 5 ml of  $\text{D}_2\text{O}$  and stirred overnight in a glove box. This solution was then lyophilized with a VirTis Lyophilizer over a period of 3 days to produce a white crystalline solid.

### Control Terms to be included

FRD-902, FRD-903, FRD-903K